Glass and Ceramics, Vol. 68, Nos. 3 – 4, July, 2011 (Russian Original, Nos. 3 – 4, March – April, 2011)

UDC 666.76

NEW TYPES OF LIGHT-WEIGHT REFRACTORY AND HEAT-INSULATION MATERIALS FOR LONG-TERM USE AT EXTREMELY HIGH TEMPERATURES

V. S. Vladimirov,[1] E. S. Lukin,[2, 4] N. A. Popova,[2, 5] M. A. Ilyukhin,[3] S. E. Moizis,[3] E. S. Moizis,[3] and M. A. Artamonov[3, 6]

Translated from *Steklo i Keramika*, No. 4, pp. 14 – 21, April, 2011.

The particulars of a technology for new types of refractory and heat-insulation materials with high porosity, which are obtained by duplicating the cellular structure of the polymer base (polyurethane foam) and using pore-forming technology based on "cold" swelling of inorganic compositions, are examined. The use of electrocorundum, periclase, spinel, and zirconium dioxide as a base permits using such materials from 1750 to 2200°C. In a number of cases the heat-insulation materials which have been developed can successfully replace corundum fiber materials.

Key words: refractories, heat-insulation materials, fiber materials, thermal conductivity, "cold" foaming, foam factor, macro- and microstructure, phosphate binder.

The development of new effective refractory and heat-insulation materials operating under extreme conditions — at high and superhigh temperatures, in corrosive gaseous media and metal melts, with large temperature gradients and under thermal shocks, with high blowing rates of single- and two-phase flows, and so on — is one of the most important problems of modern times, equally important for aerospace technology and for any civilian sector of the national economy.

The NPKF "MaVR" JSC working together with the N. É. Bauman Moscow State Technical University, the D. I. Mendeleev Russian Chemical Technical Institute, and Institute of Structural Macrokinetics and Materials Science of the Academy of Sciences of the Russian Federation in the last 10 years has been developing and introducing into various sectors of the national economy new types refractory and heat-insulation materials and coatings for use under extreme operating conditions and possessing high operating properties and characteristics as compared with existing materials.

[1] N. É. Bauman Moscow State Technical University, Moscow, Russia.
[2] D. I. Mendeleev, Russian Chemical-Technological University, Moscow, Russia.
[3] Scientific-Manufacturing-Commercial Firm "MaVR," Zhukovskii, Moscow Oblast, Russia.
[4] E-mail: lukin@rctu.ru.
[5] E-mail: ceram@rctu.ru.
[6] E-mail: mavr@progtech.ru.

Specialized technological processes based on the use of promising technologies have been developed for creating such materials [1]:

chemical pore formation (using a "cold" foaming process);

self-propagating high-temperature synthesis (SHS);

combined use of "cold" foaming and SHS;

formation of materials based on compositions made from an inorganic binder and refractory, finely milled base with the use of modifying additives, ultradisperse particles, and nanostructures; and,

use of a burn-out base for obtaining highly-porous material with a cellular structure, and so on.

These technologies made it possible to obtain a range of new types of refractories and heat-insulating materials, coatings, greases, mortars, gunite mixes, rehabilitation mixtures, glues, heat-insulating paints, and other materials for high-temperature thermal units of different kinds [2].

In the last few years the present authors have been working fruitfully to develop new types of high-porosity light-weight cellular refractory and heat-insulation materials for long-term use at extremely high temperatures (to 1800°C). These light-weight materials with cellular structure could become a worthy alternative to the very expensive corundum materials made from poly- and single-crystalline fibers and they could expand their range of practical applications considerably.

0361-7610/11/0304-0116

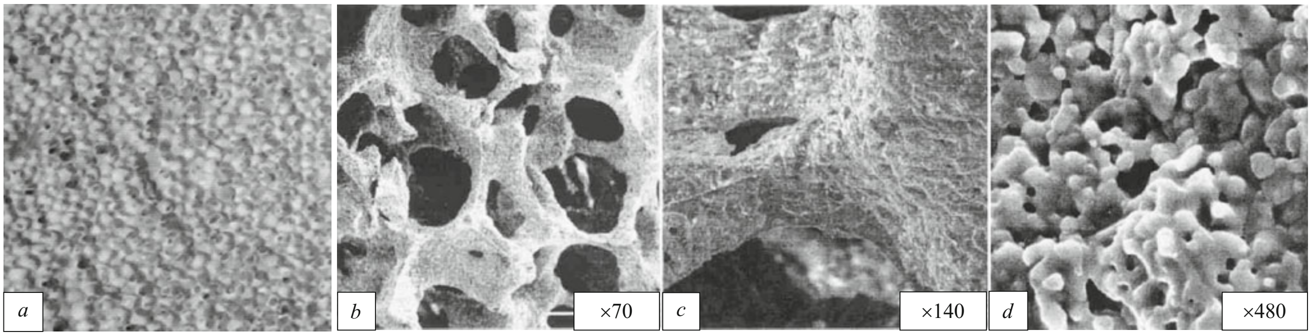

Fig. 1. Macro- (*a*) and micro- (*b*, *c*, *d*) highly porous corundum cellular materials obtained by burning out a polyurethane foam base after high-temperature firing (1600°C).

The need to develop new types of light-weight high-temperature materials is due to the fact the existing corundum fiber materials which possess undoubted advantages — low thermal conductivity, low volume mass, high heat-resistance, low accumulation of heat, and resistance to thermal shock — also have substantial drawbacks, which either make it possible to use them in an entire host of important fields or prevent their wide application in practice. The most important drawbacks of fiber corundum materials are:

– low construction strength;

– extremely high cost of the material;

– complexity and low reliability of mounting of brick material into the large lining structures in thermal units;

– large liner shrinkage during long-term service;

– high gas permeability of material and difficulty in eliminating this phenomenon;

– impossibility of using the material when it is directly exposed to any force factors and loads (contact between parts of a charge, action of fast flows of single- and two-phase gas media, flames from gas burners, metal melts, vibrations or deformations of the lining structures or framework of the thermal unit, and others).

These drawbacks make it necessary to perform research on the development of new types of high-temperature refractories and heat-insulation materials as alternatives to the existing fiber materials.

It is known that high-temperature light-weight refractories and heat-insulation materials can be developed by giving them a porous structure. This is now done by the following methods:

use of materials with a fibrous structure;

introduction of additives that burn out;

use of natural or artificial light-weight fillers;

introduction of highly porous filler or vacuum microspheres;

use of foaming;

use of evaporating liquids or special solids;

chemical pore formation;

use of a base that burns out, for example, polyurethane foam.

Analysis of all known methods of giving material a porous structure for solving the problem posed has revealed two of the most promising, in the opinion of the present authors, technologies which are based on the use of not fibrous structures but rather finely dispersed powders of heat-resistant components (electrocorundum, periclase, alumina, zirconium dioxide, and others):

– use of a burn-out base based on polyurethane foam;

– chemical pore formation based on “cold” foaming.

The first of these technologies is based on preliminary permeation of the organic materials of framework with a cellular structure (polyurethane foam) of inorganic ceramic slip followed by high-temperature firing with burn-out of the organic base material. Compositions containing electrocorundum and a small amount of alumina or periclase using a polyurethane base that burns out give highly porous (to 92%) strong articles with a cellular structure (Fig. 1) of different sizes and configurations. These articles can be used for a long time at temperature to 1800 – 1850°C.

The technology was used to obtain highly porous, rigidly formed materials (slabs, tiles, bricks, and others) with different linear dimensions and with the following properties: apparent density 350 – 450 kg/m^3; porosity 85 – 92%; pore sizes to 0.5 – 4.0 mm; compression strength 1 – 2 MPa; linear fire shrinkage 0.9 – 1.5%; thermal conductivity in the temperature range 1000 – 1600°C — λ = 0.33 – 0.35 W/(m · K); long-term use temperature 1800 – 1850°C.

Corundum tile samples with dimensions 230 × 115 × 50 mm fabricated with the proposed technology were fired in a chamber of a hearth furnace at the maximum heating temperature 1750°C and confirmed the high service properties of the material developed. This material has been in service as a replacement for corundum fiber material for more than two years as the working layer of the lining in a high-temperature electric laboratory furnace with heating temperature to 1700°C.

Covering the working surface of such a highly porous material with a dense, strong, and chemically resistant coating (protective-strengthening ceramic coating or smear) made it possible to eliminate the gas-permeability of the lining and use such especially light-weight cellular articles as a

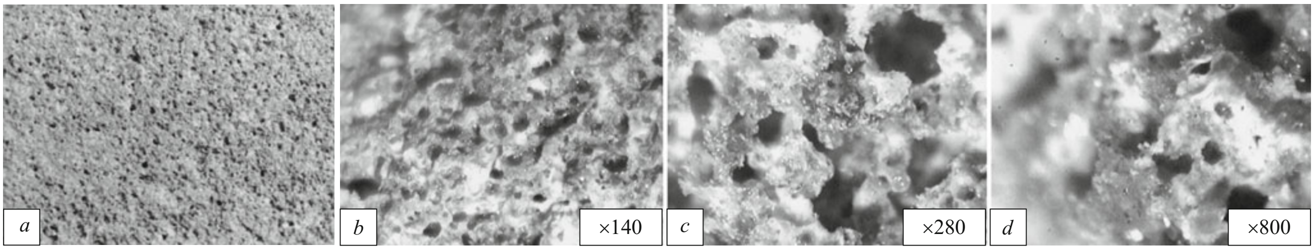

Fig. 2. Macro- (*a*) and micro- (*b*, *c*, *d*) high-temperature light-weight, rigidly formed, cellular material obtained by "cold" foaming after high-temperature firing (1600°C).

working layer for the linings of high-temperature thermal units operating in high-velocity flows of corrosive gases, liquid metals, and so forth.

The application of stabilized zirconium dioxide in the development of such materials extends the upper temperature range to 1850 – 1900°C for a thermal unit operating on air. These materials can also be used for the inner lining of vacuum furnaces with working temperature to 2200°C.

In addition, highly porous materials with cellular structure can be used successfully as filters for filtering liquid metals (iron and steel) at temperatures to 1500 – 1550°C and they can carry stationary catalysts for organic synthesis.

Of special interest for solving the problem posed — the development of new effective light-weight materials for long-term use at extremely high temperatures — is the technology of chemical pore formation based on "cold" foaming of inorganic compositions. This technology can be used to obtain highly porous rigidly formed light-weight refractory and heat-insulating materials with a cellular–grid structure [3]. Fillers, used as a base, in the form of electrocorundum, periclase, spinel, zirconium dioxide, and other refractory materials with specially chosen grain composition and different modifying additives make it possible to obtain composite ceramic materials with the required porosity, different density, low thermal conductivity, high strength, and practically no linear shrinkage during heating at high temperature and at the service temperature.

The process of "cold" foaming of inorganic compositions is conducted at room temperature without any heating or creating special conditions. The foaming effect itself is based on the chemical interaction of two or more components of a mixture with release of gaseous products of the reaction.

In such systems heterogeneous reactions proceed in the liquid phase on the surface of solid particles of one of the reagents with the release of gaseous reaction products and a large amount of heat. These reactions make it possible to room-temperature (15 – 30°C) foaming of a light-weight (ρ = 650 – 1800 kg/m^3) cellular refractory (or heat-insulating) material with the required density and prescribe service properties.

The production of finished product (cellular concretes, rigidly formed articles or intermediate products) is based on the use of dry technological mixes of different grades and compositions developed by "MaVR" JSC. With the addition of regular liquid phosphate binders these mixtures are used to fabricate by means of simple mixing apparatus a ceramic slip which is poured into casting molds, forms, or assigned cavities in lining. A short time after the slip is poured into a form (induction time of the order of 5 – 20 min) foaming of this slip starts and gaseous products of the chemical reactions are released. The foaming time depends on the chemical reagents used and the temperature of the surrounding medium and can range from 20 – 30 min to several hours (1 – 2 h and longer). A quite rapid (several minutes) process of solidification of the entire foamed slip is observed at the final stage of foaming.

The total formation time of rigidly formed materials (from start of slip preparation to completion of the solidification of the foamed slip) can be regulated and is 1 – 2 h ordinarily. The processes described form a quite strong cellular-grid structure (Fig. 2) of the light-weight rigidly formed green material of the article. It should be noted that the material contains a quite large amount of moisture (7 – 15%), some of which (3 – 5%) evaporates during the subsequent natural drying. A small linear shrinkage of the sample and considerable strengthening of the material of the article are observed.

After drying naturally (ordinarily, for at least 24 h) the green part can be, if necessary, fired at high temperature (to temperature 1550 – 1600°C). If the rigidly formed material (cellular concrete) is fabricated by casting on the site of the lining work and is used as elements of the lining structure being built (in the form of a working and/or heat-insulation layer), then the foamed material must be fired at high temperature in order to form the required phase composition and structure of the material and give it prescribed service properties. In this case the high-temperature firing must be performed as the heating unit is put into operation. In so doing, it is necessary to adhere to the special temperature regime of drying and subsequent even heating in order to put the lining structure built into the maximum operating temperature regime.

It should be note that the process of fabricating cellular concretes ready for rigidly formed articles or intermediated products made from the composition which we perfected,

performed using the “cold” foaming method, is extremely simple in practice and does not require much time or complicated, expensive equipment. Moreover, in most cases the elements of the lining of a thermal unit can also be produced directly on site by using the casting technology to pour slip either into prepared special casting molds or forms or directly on-site into assigned cavities in the lining of the thermal unit.

Studies have established that the process of “cold” foaming, in spite of its apparent simplicity, is a very complicated and quite capricious process which depends on a large number of factors: composition and concentration of individual ingredients of the reaction pair of the mixture; composition, physical-chemical properties, as well as the dispersion composition of the ingredients of a multicomponent filler; presence, composition, and properties of a modifying additive; purity of the chemical composition of the main refractory ingredients; temperature of the surrounding medium; scale factor; construction, material, and thermophysical properties of the reaction vessel (casting mold); conditions of heat transfer during foaming between the surrounding medium and the reaction vessel; nonuniformity of the volume distribution of the ingredients of the slip poured into the mold (assigned cavity). As a result, for consistent reproducibility of the main properties and characteristics of the cellular material formed in the course of “cold” foaming it is necessary to have a high production culture and to meet all requirements of the technological process exactly, including the following: accurate proportioning (weight ratios) of the liquid and solid components, use of recommended constructions for the casting forms, and ensuring that the casting work is performed under the required conditions.

The research on perfecting the required compositions and prescriptions of the initial components included comprehensive and complex studies to determine the physical-chemical, thermophysical, mechanical, and service properties and characteristics of the materials form. The following were determined during these tests:

– chemical, structural, and phase compositions of the materials formed (green samples and after high-temperature (1650°C) firing);
– volume mass of the material (green sample and after high-temperature firing);
– mass loss during calcination;
– apparent and true porosity;
– additional air and fire shrinkage;
– compression strength (green sample and after high-temperature firing);
– heat-resistance of the material;
– thermal conductivity of the material as a function of temperature.

The most important results of the studies performed to determine the main properties, characteristics, and indicators of the materials developed are presented in Table 1 and Figs. 3 – 7.

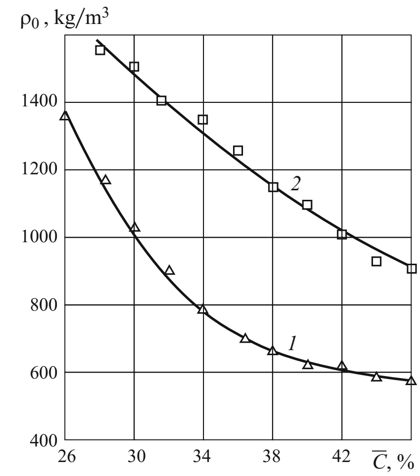

Fig. 3. Density ρ_0 of cellular material versus the relative mass $\overline{C}$ of the phosphate binder used: *1*) binder in the form of alumophosphate concentrate (APC); *2*) binder in the form of alumoborophosphate concentrate (ABPC).

Figure 3 shows a plot of the density ρ_0 of the material formed (ρ_0 is the density of the formed material in the green state) versus the relative mass C of the phosphate binder ($C = m_b / m_Z$, where m_b is the mass of the phosphate binder and m_Z is the total mass of the binder and the solid components of the slip) and the grade of the binder: APC or ABPC (APC — alumophosphate concentrate; ABPC — alumoborophosphate concentrate). Light-weight cellular materials with a wide range of apparent density can be obtained in the “cold” foaming process. The density of the formed material depends on the relative mass of the phosphate binder and its grade and can be obtained in a range of values 550 – 1600 kg/m^3 for APC and 700 – 1800 kg/m^3 for ABPC.

An important parameter for determining the required amount of the ingredients used to prepare cellular materials with the required density is the foaming factor of the slip K_f ($K_f = V_{fin} / V_{st}$, where V_{fin} and V_{st} are the final and starting volumes of the formed material, respectively). This factor is determined as the ratio of the volume of the article formed after foaming to the initial volume of the slip from which the article is made. If the dependence of this factor on the values of the obtained density of the cellular material is known, then the values of all required initial materials for forming the finished product with the required volume can be calculated. Figure 4 shows the data from processing a large number of tests to determine the foaming factor K_f of the slip as a function of the apparent density ρ_0 for different compositions of the cellular materials. This factor is in the range 1.5 – 3.5 density from 1500 to 650 kg/m^3 and is essentially independent of the composition of the initial components of the mix and the grade of the binder.

Important characteristics for any highly porous materials are the compression strength and thermal conductivity. These characteristics largely depend on the density of the materials

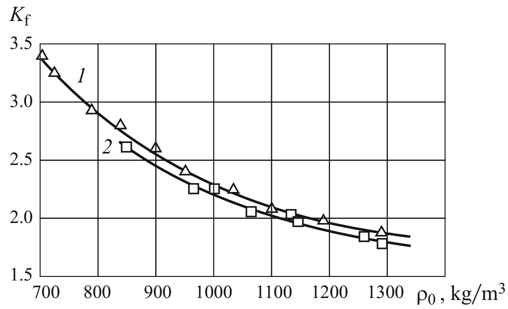

Fig. 4. Foaming factor K_f versus the density ρ of light-weight material: *1*) APC binder; *2*) ABPD binder.

and the character of their pore structure (shape, number, and size of pores, degree of pore regularity, framework structure and material, linear dimensions and wall thickness of the barriers of the framework, pore sizes in the framework material, and others). Usually, materials with high porosity and smaller cellular regular pore structure have the best characteristics.

Figure 5 shows the dependence of the compression strength σ_{com} of the cellular materials developed versus the density ρ of these materials. The materials developed possess quite high structural strength in the green and especially the fired states. After firing these materials substantially (several-fold) exceed the compression strength of existing light-weight corundum materials of the type KL-1.3 and KL-1.8 and by an even larger factor the strength of fibrous corundum materials. Such high values of the compression strength are possible for cellular materials because it became possible to form during foaming a high-quality cellular-grid pore structure and to obtain after high-temperature firing a final phase composition in the form of alumophosphates with cristobalite crystal structure.

The effectiveness and reliability of using the new type of light-weight high-temperature heat-insulating materials largely depends on its thermophysical properties, specifically, the thermal conductivity, heat capacity, and service temperature of alternative materials. In this case it is desirable to have the lowest possible thermal conductivity. It should be noted that the thermal conductivity of modern fiber corundum materials is (0.22 – 0.24) – (0.32 – 0.35) W/(m · K) in the temperature range 1000 – 1600°C.

TABLE 1. Basic Properties and Indicators of the Light-Weight Cellular Materials Developed and Fiber Articles from Corundum Fibers

Properties, parameter, indicator	Brand of foamed cellular materials			Fiber materials — slabs HT-1800
	VBF-850 KP	VBF-1000 KP	VBF-1200 KP	
Service temperature, °C:				
long time	1650	1700	1750	1750
short time	1700	1750	1800	1800
Material density, kg/m^3	800 ± 0.6%	1000 ± 0.6%	1200 ± 0.6%	520 ± 10%
Linear shrinkage, %	1.5 – 2.5	1.2 – 2.2	1.1 – 1.8	2.0 – 4.0
Compression strength, MPa	4.5 – 5.2	6.2 – 6.9	8.9 – 9.8	0.3 – 0.6
Chemical composition, %:				
SiO_2	–	–	–	10
Al_2O_3	70	74	78	90
MgO + admixtures	30	26	22	–
Mass losses, %:				
during natural drying	1.5	0.8	0.4	–
during firing of the material	11.3	9.6	9.2	–
Porosity, %:				
closed	8	10	15	–
true	69	63	56	–
Thermal conductivity, W/(m · K) at temperature, °C:				
400	0.14	0.21	0.23	0.17
800	0.17	0.24	0.3	0.22
1000	0.18	0.26	0.33	0.24
1200	0.19	0.27	0.36	0.27
Price (cost) of 1 m^3 material, USD:				
cellular concrete	3.1 – 3.5	3.5 – 4.1	4.5 – 5.2	–
slab	5.2 – 5.5	5.8 – 6.1	6.6 – 7.0	35.0 – 70.0

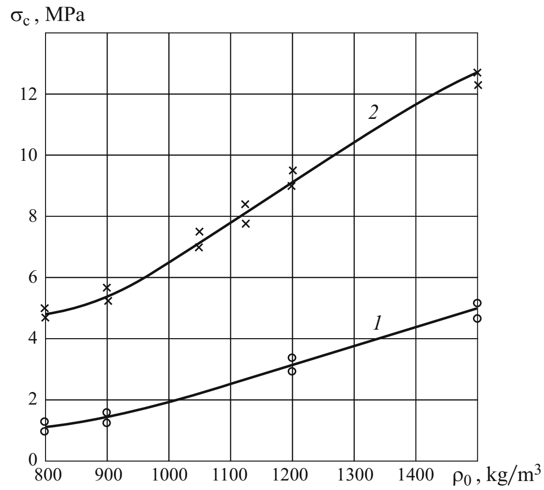

Fig. 5. Compression strength σ_{com} of light-weight cellular materials versus their density ρ: *1*) material fired at 1600°C; *2*) green (unfired) material.

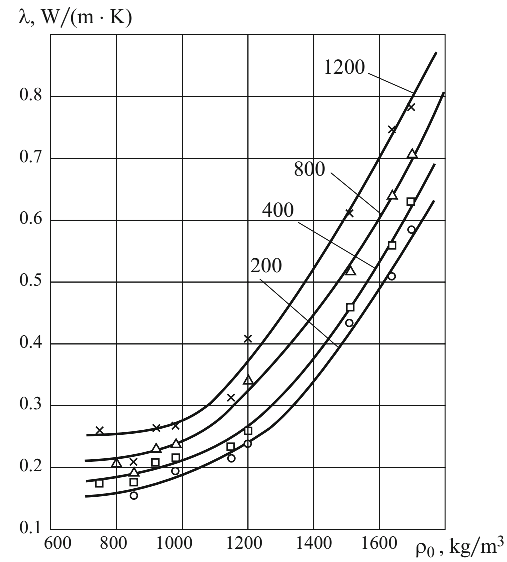

Fig. 6. Thermal conductivity λ versus the apparent density ρ of light-weight cellular materials at different temperatures (the test temperature is indicated on the curves).

Studies have shown that the thermal conductivity of cellular materials is determined not only by the total porosity, pore size and shape, and mineral composition but also largely by the pore structure formed.

The thermal conductivity versus the density of the developed corundum cellular materials at different temperatures is shown in Fig. 6, and the thermal conductivity versus the heating temperature for four value of the density (ρ = 800, 900, 100, 1200 kg/m^3) of these materials is shown in Fig. 7. The latter figure also shows the analogous values for corundum fiber materials HT-1750 and HT-1800 which are made by the firm AB UTENOS ELECTROTECNIKA (Lithuania) and whose apparent densities are 420 ± 10 kg/m^3 and 520 ± 10 kg/m^3, respectively.

For high-porosity cellular materials, the dependence of the thermal conductivity on the apparent density has a region with a flat minimum (see Fig. 6), which is observed at densities 600 – 800 kg/m^3 and at temperatures 200 – 1200°C for the compositions developed for the cellular materials corresponds to the values 0.15 – 0.25 W/(m · K).

As the apparent density of the cellular material increases to 900 – 950 kg/m^3 the thermal conductivity increases somewhat, and above 1200 kg/m^3 an intense increase of λ as a function of ρ is observed.

The values of the thermal conductivity for the developed compositions of the cellular materials with densities to 900 – 950 kg/m^3 have in the entire working temperature range (to 1750°C) somewhat lower values than the analogous parameters for corundum fiber materials with density 420 – 520 kg/m^3 (see Fig. 7), while for densities 1000 – 1100 kg/m^3 the values are practically the same as for corundum fiber materials.

Additional information on the main properties, characteristics, and indicators of the materials developed for three

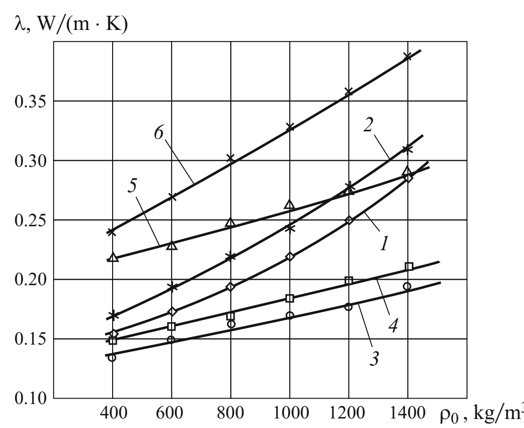

Fig. 7. Thermal conductivity λ of alternative type of high-porosity material versus the temperature: *1*) corundum fiber material HT-1750-420 (ρ = 429 kg/m^3); *2*) corundum fiber material HT-1800-520 (ρ = 520 kg/m^3); *3*) foamed cellular material VBF-800KP (ρ = 800 kg/m^3); *4*) foamed cellular material VBF-900KP (ρ = 900 kg/m^3); *5*) foamed cellular material VBF-1000KP (ρ = 1000 kg/m^3); *6*) foamed cellular material VBF-1200KP (ρ = 1200 kg/m^3).

characteristic density ranges (850, 1000, 1200 kg/m^3) are presented in Table 1. This table also gives the analogous data for fiber articles made from corundum fibers. The data in the table make it possible to compare two alternative materials with respect to the most important properties and indicators: service temperature; apparent density of the material; additional linear shrinkage; compression strength; chemical composition; mass loss on drying and firing; porosity; thermal conductivity and cost.

Analysis of the data presented clearly shows that the cellular materials developed have the best indicators with respect to important properties such as compression strength, material cost, and additional linear shrinkage.

A detailed comparative analysis of the main physical–chemical, thermophysical, mechanical, and service properties and characteristics of the materials developed and the existing fiber corundum materials made it possible to establish the advantages, virtues, and disadvantages of these materials.

The results of the analysis show that the foamed cellular materials developed at the classification temperatures and thermal conductivity compared possess the following advantages and virtues compared with the existing fiber corundum materials:

– high (more than an order of magnitude) construction strength;

– much lower (6 – 10-fold) cost of the finish product;

– smaller (by 1.5 – 2.0) additional shrinkage;

– construction simplicity and technological adaptability in constructing linings;

– possibility of fabricating ready articles (cellular concrete or green material — intermediate product) on the site of the lining construction work;

– high adhesion power of the cellular material formed to other types of lining materials used and to metal structures;

– possibility of ensuring (when necessary) protective properties and gas-permeability the surface of the working layer of the lining;

– serviceability of the structural elements of lining made of cellular concretes for long-term usage;

– possibility of used the material as a working layer of lining in thermal units, operating under moderate force loads, vibrations, fast single- and two-phase flows, flames from burners, in contact with melted metals, and so on.

The disadvantages of the materials developed with respect to the fiber corundum materials include the following: lower heat resistance and stability against thermal shocks; high heat capacity and mass characteristics of the structural elements of the lining made from cellular materials, and because of the high apparent density of the materials developed worse dynamical properties of the thermal unit when it is heated and allowed to cool.

For efficient on-site preparation of the effective light-weight cellular refractories and thermal insulation materials for extremely high temperatures and long-term operation “MaVR” JSC developed and now produces unformed materials in the form of dry technological mixtures for two different temperature ranges: 1500 – 1650 and 1600 – 1750°C.

The following brands of dry technological mixture of the type VBF (foamed concrete on phosphate binder) are now being produced:

for the temperature range 1500 – 1650°C: VBF-650K; VBF-850K; VBF-1000K; VBF-1200K; VBF-1500K; VBF-1800K (the numbers in the brands are the average value of the density of the cellular concrete);

for the temperature range 1600 – 1750°C: VBF-850KP; VBF-1000KP; VBF-1200KP; VBF-1500KP.

Work on expanding the list of high-temperature unformed materials is continuing at “MaVR” JSC. Studies on the development of new effective light-weight cellular refractory and heat-insulating materials for extremely high application temperatures with improved service properties (cellular materials with lower apparent density and higher long-term service temperature) are also being conducted.

In summary, the high-temperature cellular materials developed for use at extremely high temperatures are relatively inexpensive, highly porous light-weight ceramic materials with high structural strength and low thermal conductivity. They can be used successfully as effective materials for working and/or heat-insulating layers of linings of different types of high-temperature thermal units: electric laboratory and industrial chamber heater furnaces, tunnel firing and hearth furnaces, reactors for obtaining new materials, and others. Because of their applications technology the initial components (dry technological mixtures and regular phosphate binders) make it possible to develop structural elements of high-temperature linings with prescribed usage properties directly on site.

REFERENCES

1. V. S. Vladimirov, A. N. Galagan, M. A. Ilyukhin, et al., “New refractories and heat-insulating materials and their production technologies,” *Novye Ogneupory*, No. 1, 81 – 88 (2002).
2. M. V. Artamonov, V. S. Vladimirov, S. E. Moizis, et al., “Use of new refractories and heat-insulating materials with high application properties,” *Novye Ogneupory*, No. 9, 28 – 29 (2006).